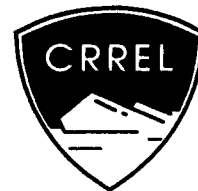


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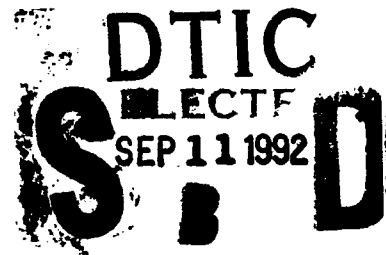


**Softening of  
Rigid Polyvinyl Chloride by  
High Concentrations of Aqueous  
Solutions of Methylene Chloride**

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Louise V. Parker, Thomas A. Ranney and Susan Taylor

May 1992

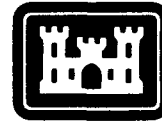


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**U.S. Army Corps  
of Engineers**  
Cold Regions Research &  
Engineering Laboratory

# **Softening of Rigid Polyvinyl Chloride by High Concentrations of Aqueous Solutions of Methylene Chloride**

Louise V. Parker, Thomas A. Ranney and Susan Taylor

May 1992

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## **PREFACE**

This report was prepared by Louise V. Parker, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division, Thomas A. Ranney, Summer Associate of the Army Research Office High School Faculty Program, and Susan Taylor, Research Physical Scientist, Geological Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding was provided by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Martin H. Stutz, Project Monitor.

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# Softening of Rigid Polyvinyl Chloride by High Concentrations of Aqueous Solutions of Methylene Chloride

LOUISE V. PARKER, THOMAS A. RANNEY AND SUSAN TAYLOR

## INTRODUCTION

Over the past few years there has been a great deal of concern over what type of materials should be used for casings and screens in groundwater monitoring wells. Most of the attention has focused on the three most commonly used materials—rigid polyvinyl chloride (PVC), stainless steel and polytetrafluoroethylene (PTFE) or Teflon. This concern arose in part from considerations raised by the Environmental Protection Agency's *Technical Enforcement Guidance Document* (TEGD). The TEGD was worried about two issues: 1) the structural integrity of these materials and 2) possible effects these materials might have on sample integrity. The TEGD noted that PVC is severely degraded when in contact with certain neat (or pure) solvents (ketones, esters and aromatic hydrocarbons) (USEPA 1986). What is less commonly understood is what effect aqueous solutions of these solvents can have on the structural integrity of PVC.

Berens (1985) examined the permeation of organic solvents in PVC pipe and found the rate of penetration changes by many orders of magnitude as the concentration or activity of the solvent in the environment is varied. According to Berens, activity and sorption isotherms represent important concepts related to the transport of a substance from one phase to another, e.g., from a vapor, groundwater or soil environment to a PVC pipe wall. The pure liquid is usually chosen as the reference state for both liquid or vapor phases and is assigned an activity of 1.0. In the vapor phase, activity is the ratio of the partial pressure  $P$  of the substance to its saturated vapor pressure  $P_0$  at the same temperature. For liquid or solid phases, activity is most simply determined by measuring the

partial pressure  $P$  of the vapor in equilibrium with that phase (activity =  $P/P_0$ ).

Berens plotted the equilibrium sorption data for a number of solvents in PVC by combining results from vapor sorption tests for a particular solvent with results from liquid sorption tests for the same solvent. PVC powders and thin film (50  $\mu\text{m}$ ) samples were used in the vapor sorption studies, while sheet samples were used in the liquid immersion tests. To obtain liquid sorption data for diluted solvent (activities less than 1.0), polyethylene glycol (PEG) was used as an inert solute or activity depressant.

Figure 1 shows the equilibrium solubility data for toluene in PVC. Berens noted that the Flory-Huggins equation (eq 1) adequately described the solubility isotherms for this solvent (Fig. 1) and a number of others in PVC. The Flory-Huggins equation relates activity (or  $P/P_0$ ) to solubility as follows

$$\ln (P/P_0) = \ln (V_1) + V_2 + \chi (V_2)^2 \quad (1)$$

in which  $V_1$  is the volume fraction of solvent in the swollen polymer and  $V_2 = 1 - V_1$  is the polymer volume fraction;  $\chi$  is the  $(V_1)$  polymer-solvent interaction parameter. ( $\chi$  can be estimated from eq 1 by using the equilibrium solubility.)

The value of  $\chi$  can be used as a measure of the swelling or solvent power of a pure liquid. In general if  $\chi$  is less than 0.5, the solvent will completely dissolve the polymer. For values greater than 0.5, the larger the number, the less the swelling power. Table 1 gives the  $\chi$  values for several organic solvents in PVC.

Figure 2 shows Flory-Huggins isotherms for various values of  $\chi$  and the softening range for PVC. From these isotherms, we see that at room

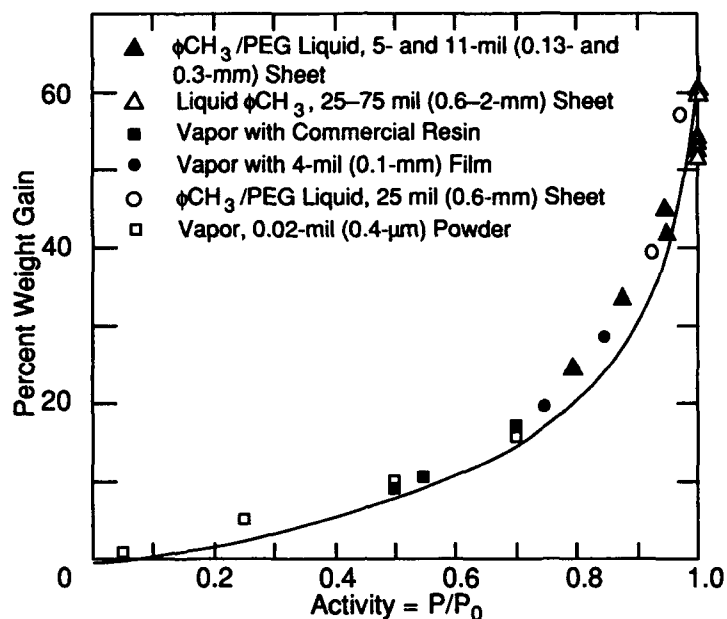


Figure 1. Solubility data for toluene in PVC at 30°C versus toluene activity  $P/P_0$  (after Berens 1985). The line is the isotherm calculated from the Flory-Huggins equation.

Table 1. Equilibrium swelling and interaction parameters for PVC-organic liquid systems (after Berens 1985).

Compound	Density (g/cm <sup>3</sup> )	Equilibrium sorption in PVC			Interaction parameter $\chi$
		Percent weight gain	Volume fraction	Time (hr <sup>a</sup> )	
Methylene chloride	1.34	>800†	>0.89	2	<0.53
Chloroform	1.49	227	0.68	6	0.64
Carbon tetrachloride	1.59	~0	~0	(280)	—
1,1-dichloroethane	1.18	132	0.61	6	<0.68
1,2-dichloroethane	1.26	700†	>0.86	6	<0.55
1,1,1-trichloroethane	1.32	67	0.42	600	0.85
1,1,2-trichloroethane	1.44	>400†	>0.80	10	<0.56
Trichloroethylene	1.47	70	0.40	5	0.88
Tetrachloroethylene	1.63	35	0.23	800	1.17
1,2-dichloropropane	1.16	176	0.68	20	0.68
Benzene	0.88	50	0.44	12	0.83
Toluene	0.87	50-60	0.45-0.49	15	0.80
Xylene	0.87	42	0.40	100	0.88
Acetone	0.79	170	0.75	2	0.61
Methanol	0.79	~1.0	—	(300)	—
Ethanol	0.79	~0.1	—	(300)	—
i-Propanol	0.79	~0.5	—	(300)	—
n-Hexane	0.66	~0.6	—	(160)	—
Vinylchloride	0.89	30	0.33		0.98

<sup>a</sup>Time to apparent equilibrium, 24-mil (0.6 mm) PVC sheet, or duration of experiment in parentheses.

†Soluble.

temperature, rigid PVC will be softened only by strong solvents (for  $\chi = 0$ ) at activities greater than 0.5. More realistically, many solvents are marginal PVC solvents but strong swelling agents, having  $\chi$  values that range from 0.5 to 1.0, and thus would cause softening at activities of 0.65 or higher.

For aqueous solutions, Berens (1985) noted that solvent activity can be approximated by dividing the concentration of the compound in solution by its solubility. Thus, for solvents dissolved in water to cause swelling or softening of rigid PVC, the pure solvent must be able to completely dissolve PVC and must exist in the environment at a concentration that exceeds one-half its solubility in water.

Olson et al. (1987) also looked at the permeation of organic solvents through PVC pipe. They tested for permeation of two neat solvents, toluene and 1,1,1-trichloroethane (TCA), through PVC pipe at room temperature. They found no breakthrough of TCA after 180 days but found softening and breakthrough of toluene after 37–41 days. They discovered that permeation by toluene was considerably slower when the pipe was exposed to a saturated (aqueous) solution of toluene, breakthrough time being 70 days. They also determined the diffusivity of toluene in PVC powders at vapor activities of 0.25 and concluded the rate of diffu-

sion was so slow that PVC pipe of 0.3-cm wall thickness would not be penetrated for over 100,000 years. They concluded that PVC was an effective barrier against swelling solvents such as toluene when the activity was low (less than 0.25) and that PVC should not be exposed to high activities (1.0) of swelling agents.

Since virtually no study has been reported using varying activities of solvents in aqueous solutions, this study was conducted to see if the relationships developed by Berens were valid for activities of solvents in aqueous solutions. Methylene chloride was selected for this study because it was one of the best solvents of PVC among those tested by Berens.

## MATERIALS AND METHODS

Pieces of rigid PVC were cut from 2-in. (5.1-cm) schedule 40 pipe. The overall dimensions of the pieces were approximately  $11 \times 4 \times 0.6$  mm ( $L \times W \times H$ ), giving a total surface area of approximately  $1.0 \text{ cm}^2$  and an approximate weight of 0.37 g. Special care was taken to eliminate contamination from grease or oil during the cutting procedure and all samples were handled using stainless steel forceps.

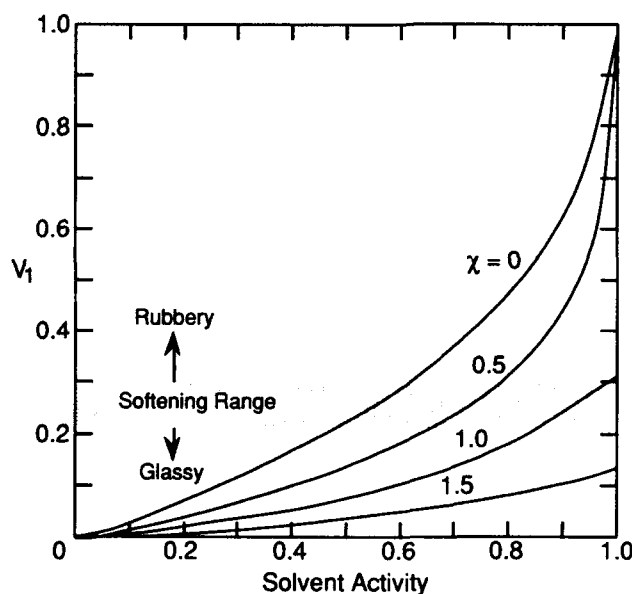


Figure 2. Flory-Huggins isotherms for various values of  $\chi$  and approximate composition for softening of PVC at room temperature (after Berens 1985).



**Table 2. Activities\* of methylene chloride and associated concentrations.**

Activity	1.0	0.8	0.6	0.4	0.2
Concentration (mg/L)	16,700	13,400	10,000	6,680	3,340

\*Activity was determined by taking the concentration of MC in solution and dividing by the solubility of MC as found in Montgomery and Welkom (1990).

The pieces of PVC were exposed to aqueous solutions of methylene chloride (MC) at five activities—1.0, 0.8, 0.6, 0.4 and 0.2—and to blanks with water only (activity = 0.0). Table 2 gives the concentration of MC for each activity. The solutions were made up in 22-mL borosilicate glass vials with aluminum lined (Teflon backed) plastic caps. The vials were filled almost to the top with Milli-Q water, MC was added using a microliter syringe and the weight of added MC was recorded. The vials were then filled to capacity with water to eliminate any headspace, capped and placed on a wrist-action shaker for 30–48 hours to assure mixing of the solvent–water phases. Vials were checked visually to determine that no small droplets of solvent remained undissolved. After mixing, the vials were opened, and previously weighed and measured pieces of PVC were added to the solutions. The length, width and thickness of each piece had been determined using a Fowler Ultra-cal II digital vernier caliper. Additional water was added to assure that there was no headspace and the vials were recapped.

For each sampling period and activity, there were three replicate samples. Samples were exposed to the solution for 4, 8, 15, 22 and 33 days. On days 4 and 8, an aliquot of solution was removed from each vial for analysis to determine loss of MC from solution during exposure. The pieces of PVC were then removed from solution, placed on paper towels and allowed to air dry for 1 hour before weighing. The length, width and thickness of each piece of PVC were measured. Observations were made of the curvature of each piece. The pieces were also tested for flexibility by holding the piece of PVC with forceps and noting the amount of force necessary to bend the sample. An unexposed, original piece of PVC was used as the reference. Samples taken on days 15, 22 and 33 were treated similarly except that the loss of MC from solution was not determined. Also, each week the remaining pieces of PVC were placed into freshly prepared MC solutions and returned to storage. Thus, no PVC piece stayed in any

solution longer than 8 days. This was done to maintain solvent stress on the PVC and thereby allow maximum sorption.

Analytical determination of MC concentrations was by Reversed-Phase High Performance Liquid Chromatography (RP-HPLC) following dilution of the aliquots 1:1 with methanol. A modular system was employed, consisting of a Spectra Physics isocratic pump with a 10- $\mu$ L loop injector, a Waters 410 differential refractometer detector with a column heater operating at 35°C, and a Hewlett-Packard 3390A digital integrator. Separation was obtained on a 25-cm  $\times$  4-mm (5- $\mu$ m) LC-18 column (Supelco) eluted with 1.5 mL/min of 1:1 (V/V) methanol–water. The retention time for the MC was approximately 4 minutes. Detector response was obtained from the digital integrator operating in the peak height mode. Two sets of MC standards were used on each sampling day. The MC standards were made up in methanol and stored in a freezer. The standards were warmed to room temperature and diluted 1:1 with water just prior to use.

In addition to measuring the macroscopic changes of the PVC (i.e., changes in dimensions, flexibility and curvature), microscopic changes in the structure of the samples were looked for using a Hitachi 500S Scanning Electron Microscope (SEM). Elemental composition was determined by using the attached Energy Dispersive X-ray Analyzer (EDAX). To avoid damaging the PVC, a thin coating of gold was deposited onto the sample's surfaces using a HUS-5GB vacuum evaporator and a fairly low acceleration voltage (15 keV) was used. Samples immersed in solutions at 0.0 (blank), 0.2, 0.6 and 1.0 activity for 4, 8, 15, 22 and 33 days were studied and photographed at three different magnifications,  $\times 30$ ,  $\times 200$  and  $\times 2000$ . Samples placed in pure methylene chloride for 15, 30, 60 and 240 minutes were also examined after drying for approximately 30 minutes.

Several statistical analyses were performed on the increase in length data. For each sample day, the data set was first tested for homogeneity of the

**Table 3. Changes in length (percent increase) of PVC pieces with time.**

Activity	Day 4	Day 8	Day 15	Day 22	Day 33
0	0.18 0.09 <u>0.09</u>	0.18 0.36 <u>0.27</u>	0.63 0.18 <u>-0.18</u>	-0.09 0.45 <u>0.18</u>	0.54 0.18 <u>0.36</u>
$\bar{X}$	0.12	0.27	0.21	0.18	0.36
02	0.72 0.82 <u>0.27</u>	-0.45 0.45 <u>0.27</u>	0.54 0.54 <u>0.63</u>	0.81 0.63 <u>0.45</u>	1.09 0.72 <u>0.36</u>
$\bar{X}$	0.60	0.09	0.57	0.63	0.72
04	0.27 0.36 <u>0.18</u>	-0.54 0.18 <u>-0.09</u>	0.18 0.00 <u>-0.27</u>	0.45 0.54 <u>0.45</u>	0.63 0.90 <u>0.54</u>
$\bar{X}$	0.27	-0.15	-0.03	0.48	0.69
06	0.54 0.54 <u>0.54</u>	0.45 0.27 <u>0.27</u>	0.63 0.27 <u>0.36</u>	1.36 0.71 <u>1.00</u>	0.45 0.36 <u>0.72</u>
$\bar{X}$	0.54	0.33	0.42	1.02	0.51
08	1.17 1.08 <u>1.26</u>	1.36 0.45 <u>0.90</u>	1.72 0.90 <u>-0.62</u>	1.62 1.52 <u>1.80</u>	1.18 3.24 <u>1.89</u>
$\bar{X}$	1.17	0.90	0.66	1.65	2.10
10	1.26 2.33 <u>-0.27</u>	0.63 1.44 <u>-0.80</u>	1.87 0.09 <u>2.08</u>	3.19 1.99 <u>2.82</u>	2.88 1.54 <u>1.34</u>
$\bar{X}$	1.11	0.42	1.65	2.67	1.53

variances using Bartlett's test. A one-way Analysis of Variance test (ANOVA) was then conducted to determine if any significant differences, at the 95% confidence level, existed among the means of samples exposed to different activity solutions for that day. When significant differences were found, a Least Significant Difference (LSD) was calculated to determine which means were significantly different.

## RESULTS AND DISCUSSION

The size, flexibility, curvature, weight and appearance of rigid PVC all changed with exposure to aqueous MC solutions. The degree of change in these characteristics was associated with solvent activity and time of exposure.

The percent changes in length of PVC as a function of time and solution activity are shown in Table 3. These data were at times highly variable. This was especially true for the samples exposed

to the highest activity solutions (1.0), where softening made it difficult to get accurate measurements. In fact, Bartlett's test for homogeneity of the variances indicated that the variances for the data on days 4, 8, 15 and 33 were not homogeneous (Table 4). As a result of this large variability, ANOVA tests indicated that there was no significant difference between samples exposed to different activities on days 4, 8 and 15 (Table 4). The variances for the data on day 22 were homogeneous and the samples exposed to the higher activity solutions (0.6, 0.8 and 1.0) were significantly greater (i.e., more swollen) than the controls (Table 4). In spite of the large variability in the variances for the data for day 33, samples exposed to the 0.8 and 1.0 activity solutions were significantly larger than the controls (Table 4). When data for the samples exposed to the 1.0 activity solutions were eliminated from the first three data sets (these samples also had the greatest variability), Bartlett's test then revealed homogeneous variances, and ANOVA tests on these smaller sets

**Table 4. Summary of statistical analyses on length data.**

Day	Bartlett's test for homogeneity of variances	ANOVA test	LSD test*
4	No	NS	
8	No	NS	
15	No	NS	
22	Yes	HS	0.0 <sup>a</sup> 0.4 <sup>a,b</sup> 0.2 <sup>a,b</sup> 0.6 <sup>b</sup> 0.8 <sup>c</sup> 1.0 <sup>d</sup> (0.18)(0.48)(0.63)(1.02)(1.65)(2.66)
33	No	HS	0.0 <sup>a</sup> 0.6 <sup>a</sup> 0.4 <sup>a</sup> 0.2 <sup>a</sup> 1.0 <sup>b</sup> 0.8 <sup>b</sup> (0.36)(0.51)(0.69)(0.72)(1.53)(2.10)
4 revised†	Yes	HS	0.0 <sup>a</sup> 0.4 <sup>a</sup> 0.6 <sup>b</sup> 0.2 <sup>b</sup> 0.8 <sup>c</sup> (0.12)(0.27)(0.54)(0.60)(1.17)
8 revised†	Yes	HS	0.4 <sup>a</sup> 0.2 <sup>a</sup> 0.0 <sup>a</sup> 0.6 <sup>a,b</sup> 0.8 <sup>b</sup> (-0.15)(0.27)(0.27)(0.33)(0.90)
15 revised†	Yes	NS	

\*Values with the same letter are not significantly different at the 95% confidence level. The mean percent increase in length is given in parentheses.

†Data were revised by eliminating data for those activities with large standard deviations.

of data revealed a significant difference between samples exposed to different activity solutions on days 4 and 15. The results of the Bartlett's, ANOVA and LSD tests on the revised data sets are also given in Table 4. On day 4, while the percent increase in length was not significantly different from the control samples for samples exposed to the 0.4 activity solution, it was for samples exposed to the 0.2, 0.6 and 0.8 activity solutions. The percent length increases for the 0.8 samples were also significantly greater than the 0.6 and 0.2 data. On day 8, the samples exposed to the 0.8 activity solutions were significantly greater than the controls, while those exposed to the 0.4, 0.2 and 0.6

activity solutions were not. On day 15, there still was no significant difference between samples exposed to the 0.2, 0.4 and 0.6 solutions and the controls. These data clearly show a statistically significant increase in length for the samples exposed to the 0.8 and 1.0 activities. In two instances, samples exposed to the 0.6 activity solutions were significantly larger than the controls, but this was never a consistent trend.

The flexibility ratings for samples after soaking are given in Table 5. High activities of solvent (1.0 and 0.8) softened the PVC so that it could be bent back over itself within 4 and 15 days respectively. By the end of the experiment (33 days), the 0.4 and

**Table 5. Observed changes in flexibility\* of PVC samples.**

Time (days)	Activity				
	0.2	0.4	0.6	0.8	1.0
4	0	0	0	1	2
8	0	0	0	1	2
15	0	0	1	2	2
22	0	0	1	2	2
33	0	1	1	2	2

\*Rankings: 0—no noticeable flexibility; 1—more flexibility than original; 2—can be bent back over itself.

**Table 5. Observed changes in curvature \*of PVC samples.**

Time (days)	Activity				
	0.2	0.4	0.6	0.8	1.0
4	0	0	0	1	2
8	0	0	1	1	2
15	0	0	1	1	2
22	0	0	1	2	2
33	0	1	1	2	2

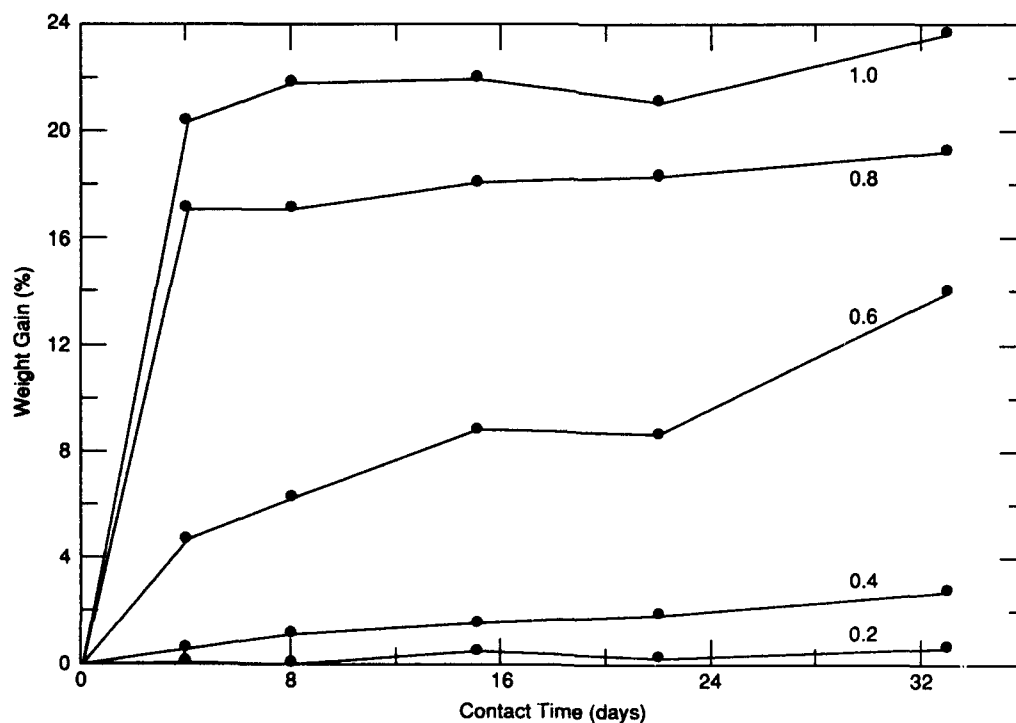
\*Rankings: 0—no noticeable curvature or twisting; 1—some curvature or twisting in at least one of the three samples; 2—obvious curvature or twisting in at least two of the three samples

0.6 activities showed only marginal softening, while there was no noticeable change in flexibility at the 0.0 or 0.2 activity.

The PVC pieces were also observed for changes in curvature or twisting (Table 6). Only the pieces exposed to the highest activities (0.8 and 1.0) showed obvious twisting in two or more of the three samples. This was noted after only 4 days for samples in the 1.0 activity solution and after 22 days for samples in the 0.8 activity solution. By the end of the experiment, the samples in the 0.2

activity solutions showed no curvature, while at least one of the three samples in the 0.4 and 0.6 activity solutions appeared to show some curvature or bending.

The differences in the change in weight of PVC was perhaps the most striking difference between samples at different activities (Fig. 3). Samples exposed to the high activity (1.0 and 0.8) solutions had a large, rapid increase in weight (17 and 20% after 4 days), which then leveled off. For samples exposed to the 0.6 activity, initial weight increases



**Figure 3. Weight gain by PVC at various activities of methylene chloride vs time.**

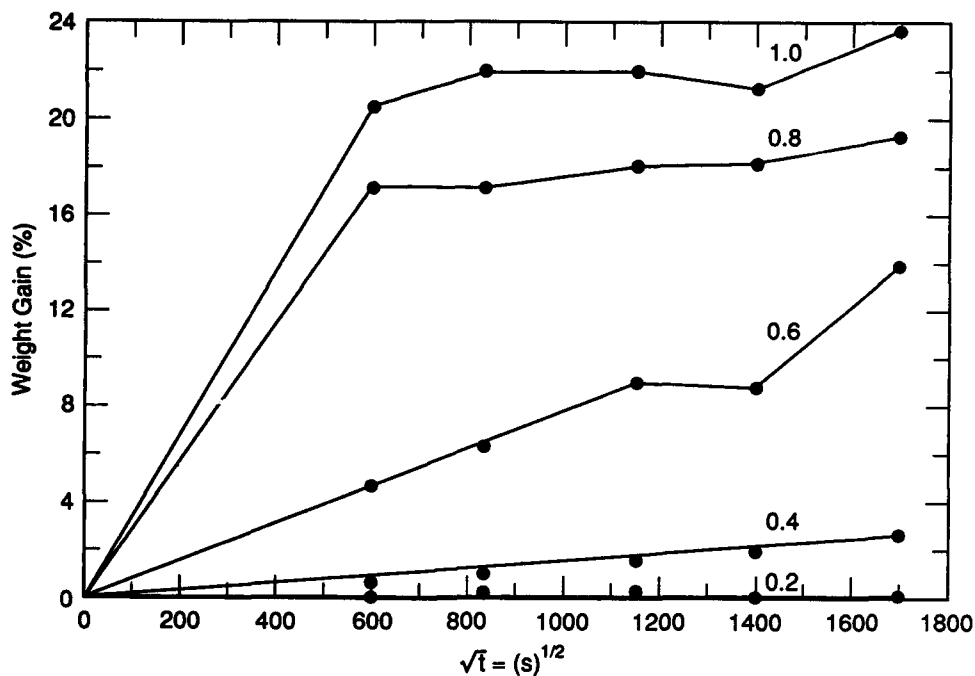


Figure 4. Weight gain by PVC at various activities of methylene chloride vs  $t^{1/2}$ .

were less dramatic, but it continued to increase, reaching a total of 14%. For samples exposed to the 0.4 activity solutions, the pieces of PVC gained weight slowly throughout the entire study. Samples exposed to the lowest activity solution (0.2) showed a slight but measurable weight gain (0.8%) by the end of the study. For the control samples (0.0 activity), the weight gain was 0.1% by the end of the experiment. Figure 4 shows a plot of the percent gain in weight vs  $t^{1/2}$  (with time in seconds). As Berens found in his study, there is a dramatic difference in rate associated with activity. According to Berens, for the kinetics to be Fickian, this plot should be linear for the first half of the sorption process, then asymptotically approach the equilibrium uptake. The kinetics for sorption of MC by PVC at 0.6, 0.4 and 0.2 activity initially appear to be Fickian. While there are not enough early data ( $t^{1/2} < 500$ ) for the higher activities (0.8 and 1.0) to be certain, the kinetics appear to be similar to those found in Figure 5 for samples of PVC exposed to trichloroethane (TCA) at the 0.8 activity. Berens described this behavior as non-Fickian. These results agree well with Berens' findings that the kinetics for sorption is Fickian for low activity solutions (less than 0.5) and non-Fickian for high activity solutions (1.0 and 0.8). When diffusion is Fickian (e.g., with low activity solutions), diffusivities can be determined

and this allows for permeation to be predicted for thick-walled pipe.

For samples taken on days 4 and 8, the amount of MC remaining in solution after exposure to PVC was determined. Total losses of MC on a mass basis were much greater than could be accounted

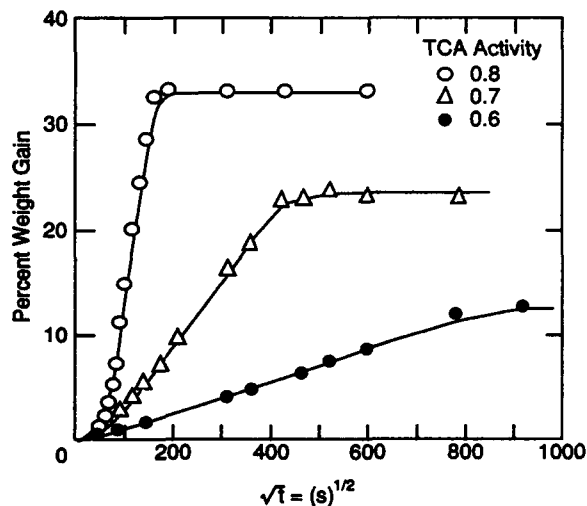
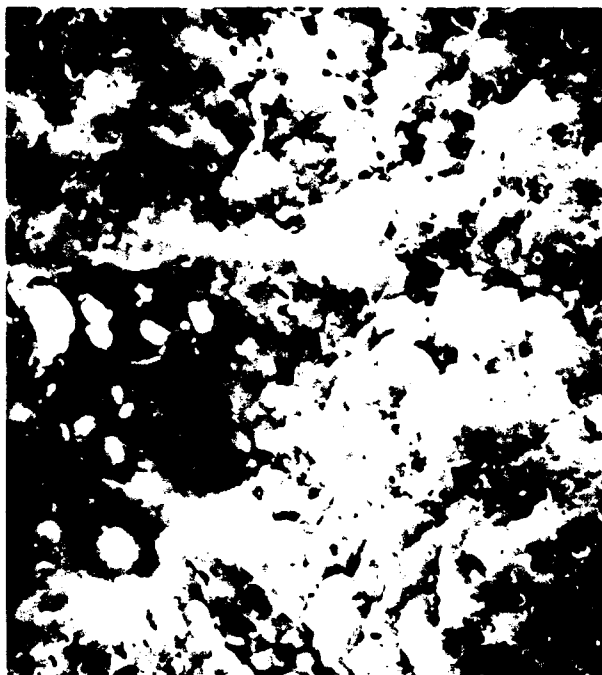


Figure 5. Weight gain versus  $t^{1/2}$  for liquid immersion of a 0.3-mm PVC sheet in trichloroethylene-polyethylene glycol mixtures at indicated activities (after Berens 1985).



*a. After 15 minutes.*



*b. After 30 minutes.*

*Figure 6. Scanning electron microscope photos of PVC in pure methylene chloride ( $\times 2000$ ).*

for by the weight gained by PVC. Four-day-old solutions with no PVC (blanks) showed a range in the mean loss of MC from 1.22 to 4.64% and the 8-day solutions showed a range in the mean loss from 11 to 24% (Appendix A). The variation in MC lost between replicates was so large that we discontinued these analyses. The variability in this loss was most likely caused by differences in headspace (although we tried to have none) or in the tightness of the caps, or both.

The SEM photos show that samples placed in pure MC have a very different surface texture than those placed in aqueous solutions of MC. Figures 6a and b show a hummocky surface filled with small holes that is characteristic of the samples placed in pure solvent. Although samples placed in aqueous solutions of MC have a range of surface textures (see Fig. 7a–d), none show the hummocky texture. In spite of the obvious softening at the higher activities, there does not appear to be any clear change in the texture of these samples that can be associated with increasing activity or solvent concentration. Linear surface features, which apparently resulted from cutting of these samples, can be seen in all samples placed in the aqueous solutions but not in those exposed to neat solvent (Appendix B). These observations agree well with similar observations made by us previously (Tay-

lor and Parker 1990). Using an SEM at that time, we found no change in the appearance of PVC chips exposed to an aqueous solution of four organics (toluene, tetrachloroethylene and o- and p-dichlorobenzene), each with an initial activity of 0.25, after soaking for 6 months.

Samples left 15 days or longer in 1.0 solutions had small, triangularly shaped deposits on their surfaces (Fig. 7d). We believe that these deposits are a product of the interaction between MC and the aluminum cap liners, as EDAX analyses of these deposits indicate they contain Cl, Al and a trace amount of Ca. When the cap liners were examined, all except those from the control samples (with no MC) had clusters of similarly shaped triangles on the Al (see Fig. 8). Also, vials with Al-lined caps containing a solution of MC at an activity of 1.0, but no PVC, also had similarly shaped deposits on the cap liners.

## CONCLUSIONS

According to Berens' predictions, methylene chloride (MC) should not soften PVC at activities below 0.5 (Berens 1985). Early in this study, there was obvious softening of PVC at the 0.8 and 1.0 activities. These samples showed rapid weight



*a. In 0.0 activity solution.*



*b. In 0.2 activity solution.*



*c. In 0.6 activity solution.*



*d. In 1.0 activity solution.*

*Figure 7. Scanning electron microscope photos of PVC after 33 days ( $\times 2000$ ).*



a. At  $\times 200$ .



b. At  $\times 2000$ .

Figure 8. Scanning electron microscope photos of aluminum cap liner.

gain, obvious curvature or twisting, were easy to bend and were significantly longer than control samples.

By the end of this experiment, it was clear that at the 0.2 activity there was no sign of softening or swelling. The results at the intermediate activities (0.4 and 0.6) are less clear. These samples did appear somewhat less rigid and at least one sample (out of three) exposed to both the 0.4 and 0.6 activity solutions showed some bending by the end of the experiment. With respect to an increase in size, the samples exposed to the 0.4 solutions were never significantly different from the control samples. While the samples exposed to the 0.6 activity solutions were significantly different from the controls on two occasions (days 4 and 22), there was never a consistent pattern with time.

The SEM micrographs showed distinct differences in surface textures between samples placed in pure MC and those placed in aqueous solutions of MC. Among those samples exposed to aqueous solutions of MC, there did not appear to be any clear changes in texture that could be associated with increased activity (or concentration of solvent) in spite of obvious softening in these samples. Therefore, the dramatic change in surface structure seems to correlate with the large differences in weight gain and swelling associated with PVC

exposed to neat solvent vs aqueous solutions. Berens noted that at equilibrium, the percent weight gain by PVC exposed to neat MC was more than 800%, while we observed only a 25% weight gain in PVC exposed to a solution with an approximately 1.0 activity. The amount of swelling is also considerably less for PVC samples exposed to aqueous solutions than those exposed to neat solvents.

None of our findings indicated any softening (changes in curvature and flexibility) at the 0.2 activity. Only our most subjective findings indicated some possibly slight change at the 0.4 activity. The same was true at the 0.6 activity, except that samples were significantly larger than the controls in two instances. However, it is clear that at 0.8 and 1.0 activities PVC can be softened. It is hard to know for certain whether the changes that we saw at the intermediate activities were really indicative of softening and swelling. However, being conservative, we can safely say that solutions of MC at activities 0.2 and below will not cause softening of rigid PVC pipe. These results agree reasonably well with the predictions of Berens. Berens predicted that a solvent such as MC with an interaction parameter ( $\chi$  value) of less than 0.53 will cause softening only at activities of 0.5 or higher. The slight differences between our find-



ings and those of Beren's may be attributable to differences in the affinity of the MC molecule for aqueous solution vs polyethylene glycol, which Berens used as an activity depressant. Partitioning of MC by the polymer would be more strongly favored in an aqueous solution than it would be in a solution with polyethylene glycol.

An activity of 0.2 corresponds to a very high concentration: 3340 mg/L. Thus, in most environmental situations, aqueous concentrations of MC, or any other solvent, will not cause serious swelling or softening of PVC pipe.

#### LITERATURE CITED

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*can Water Works Association*, November, pp. 57-65.

**Montgomery, J.H. and L.M. Welkom** (1990) *Groundwater Chemicals Desk Reference*. Chelsea, Michigan: Lewis Publishers, Inc.

**Olson, A.J., D. Goodman and J.P. Pfau** (1987) Evaluation of permeation of organic solvents through PVC, asbestos/cement, and ductile iron pipes. *Journal of Vinyl Technology*, 9(3): 114-118.

**Taylor, S. and L. Parker** (1990) Surface changes in well casings pipe exposed to high concentrations of organics in aqueous solution. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 90-7.

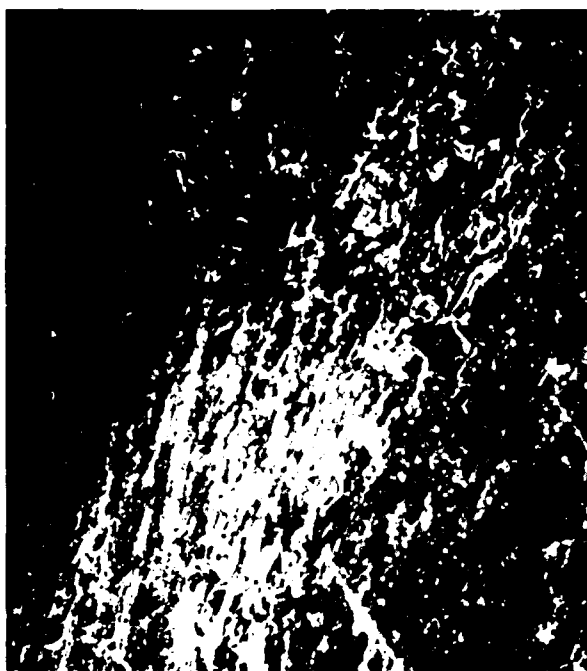
**U.S. Environmental Protection Agency** (1986) Resource Conservation and Recovery Act (RCRA) ground-water monitoring technical enforcement guidance document. Washington, DC: U.S. Government Printing Office.

**APPENDIX A: PERCENT LOSS OF METHYLENE CHLORIDE IN CONTROL SAMPLES.\***

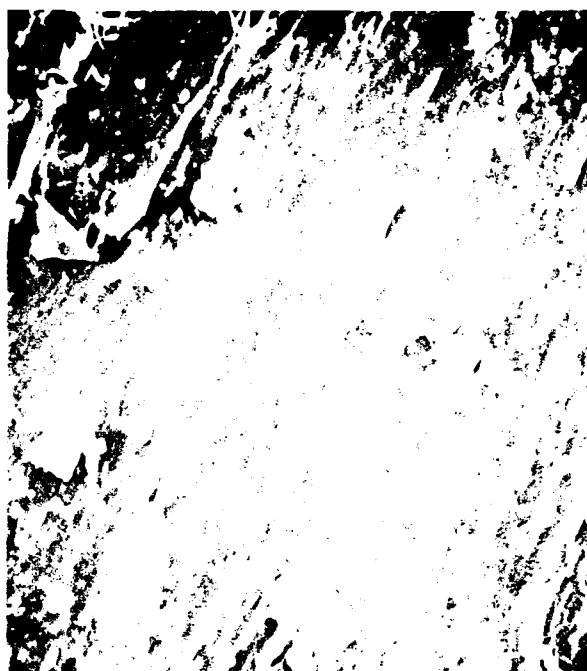
<i>Activity</i>	<i>4 days</i>	<i>8 days</i>
0.2	0.90	21.4
	1.53	15.5
	<u>      </u>	<u>20.3</u>
	$\bar{X} = 1.22$	$\bar{X} = 19.1$
0.4	2.05	16.5
	3.61	5.59
	<u>0.91</u>	<u>10.3</u>
	$\bar{X} = 2.19$	$\bar{X} = 10.8$
0.6	1.41	30.7
	2.15	23.8
	<u>2.57</u>	<u>17.7</u>
	$\bar{X} = 2.04$	$\bar{X} = 24.1$
0.8	4.27	16.1
	2.44	37.2
	<u>5.14</u>	<u>17.5</u>
	$\bar{X} = 3.95$	$\bar{X} = 23.6$
1.0	6.05	25.4
	4.77	43.7
	<u>3.09</u>	<u>38.5</u>
	$\bar{X} = 4.64$	$\bar{X} = 24.3$

\*Samples with no PVC.

APPENDIX B: SCANNING ELECTRON MICROSCOPE PHOTOS.



1.  $\times 30$ .



2.  $\times 200$ .



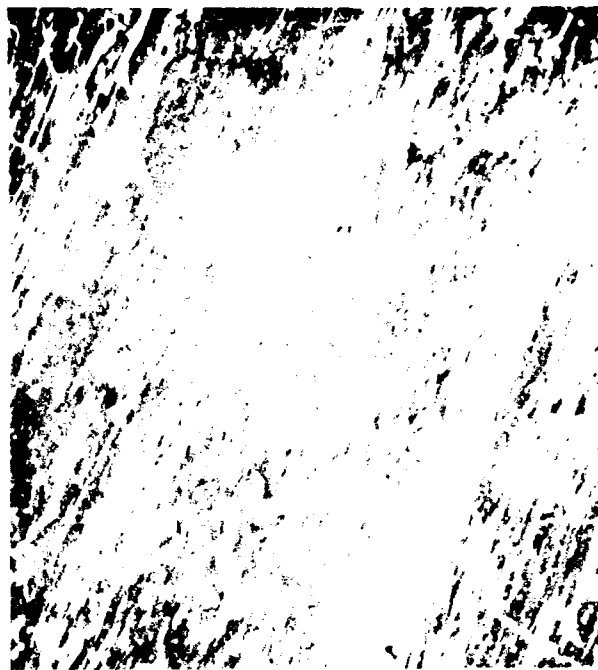
3.  $\times 2000$ .

*a. In 0.0 activity solution.*

*Figure B1. Scanning electron microscope photos of PVC after 4 days.*



1.  $\times 30$ .



2.  $\times 200$ .



3.  $\times 2000$ .

*b. In 0.2 activity solution.*

*Figure B1 (cont'd). Scanning electron microscope photos of PVC after 4 days.*



1.  $\times 30$ .



2.  $\times 200$ .



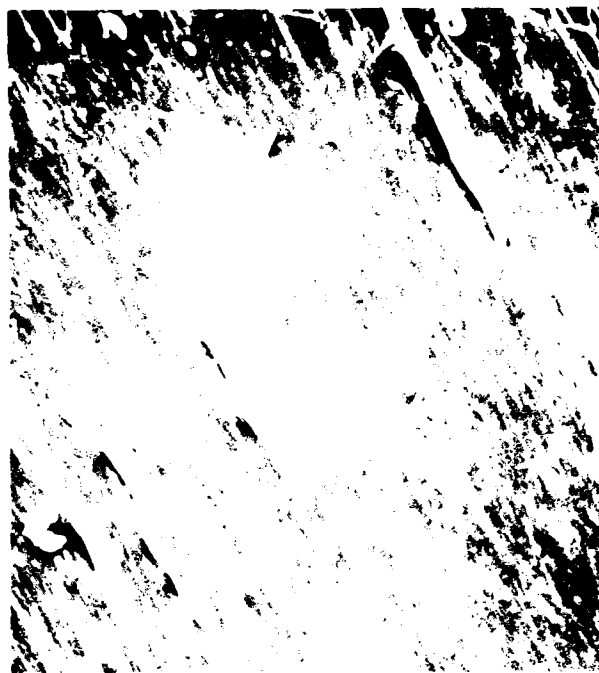
3.  $\times 2000$ .

*c. In 0.6 activity solution.*

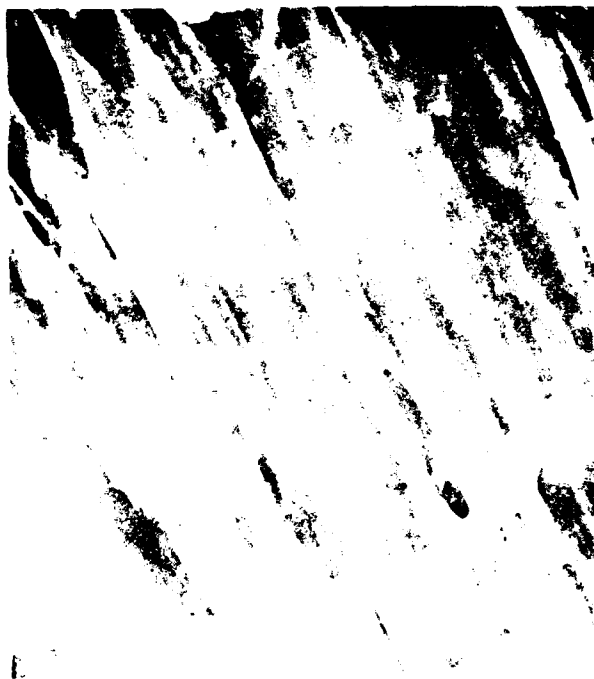
*Figure B1 (cont'd).*



1.  $\times 30$ .



2.  $\times 200$ .



3.  $\times 2000$ .

*d. In 1.0 activity solution.*

*Figure B1 (cont'd). Scanning electron microscope photos of PVC after 4 days.*



1.  $\times 30$ .



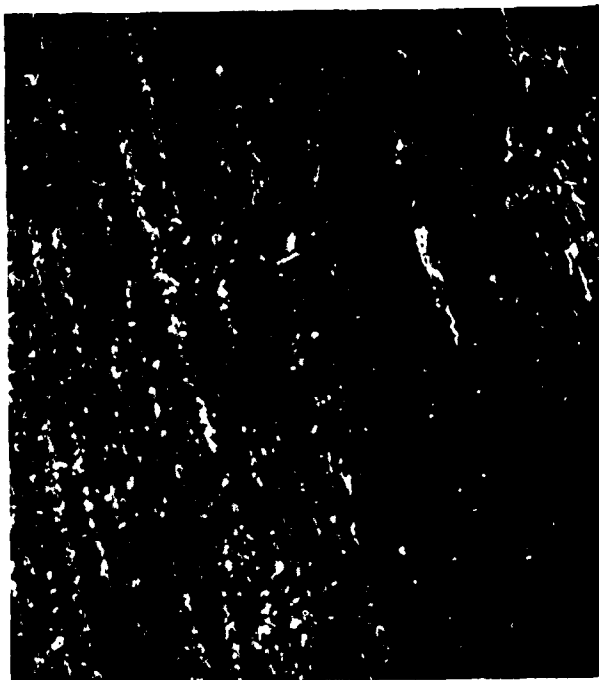
2.  $\times 200$ .



3.  $\times 2000$ .

*a. In 0.0 activity solution.*

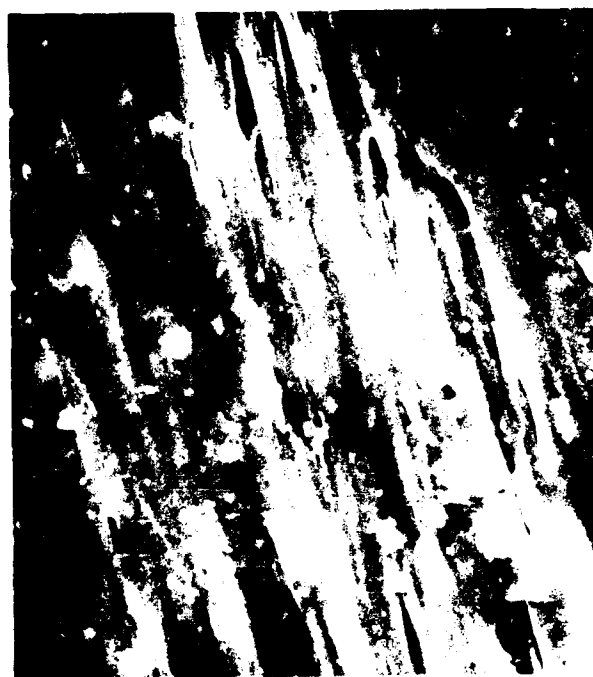
*Figure B2. Scanning electron microscope photos of PVC after 8 days.*



1.  $\times 30$ .



2.  $\times 200$ .

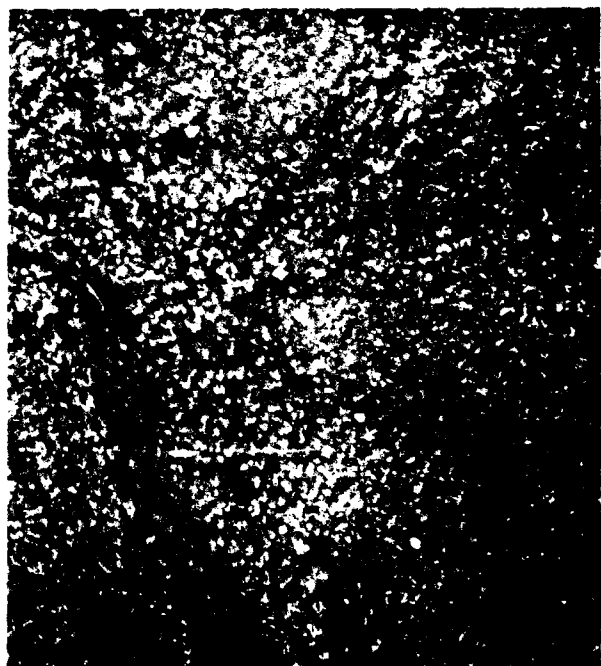


3.  $\times 2000$ .

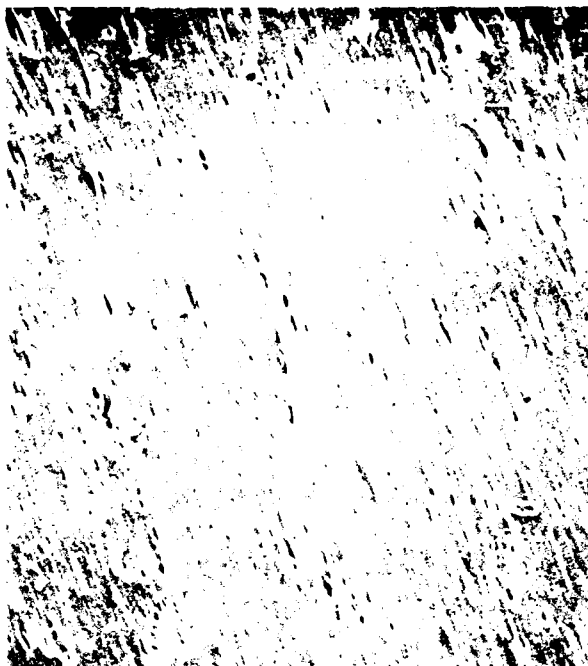
*b. In 0.2 activity solution.*

*Figure B2 (cont'd). Scanning electron microscope photos of PVC after 8 days.*





1.  $\times 30$ .



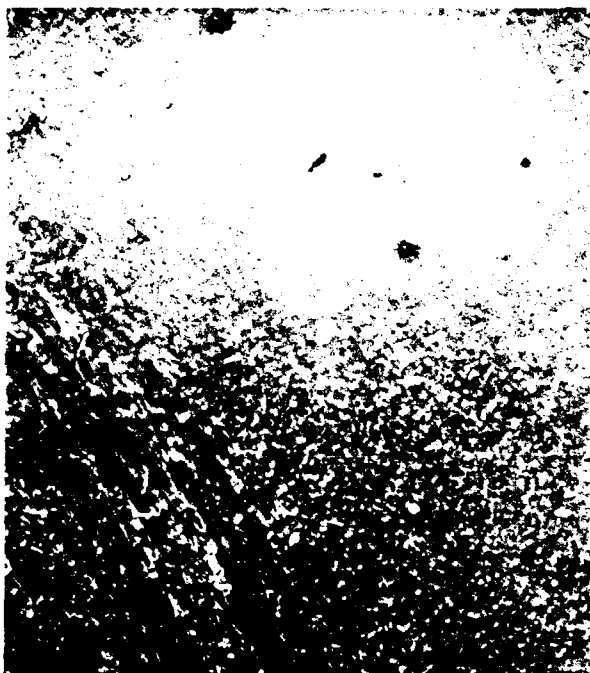
2.  $\times 200$ .



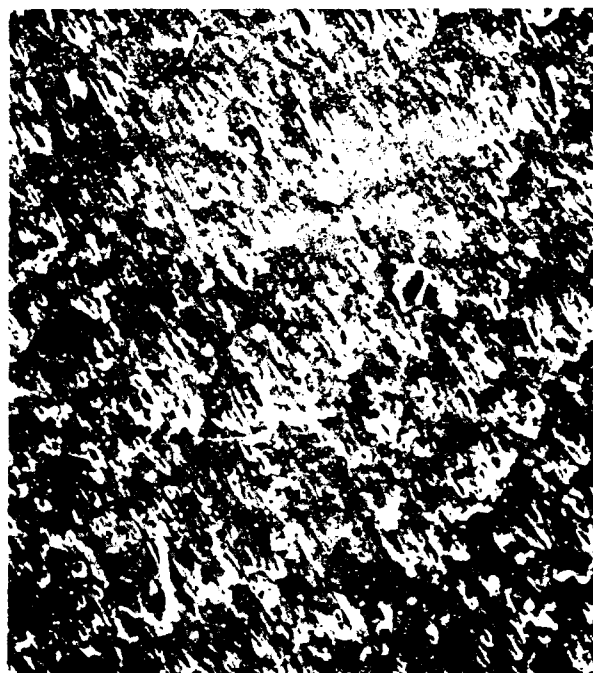
3.  $\times 2000$ .

*c. In 0.6 activity solution.*

*Figure B2 (cont'd).*



1.  $\times 30$ .



2.  $\times 200$ .



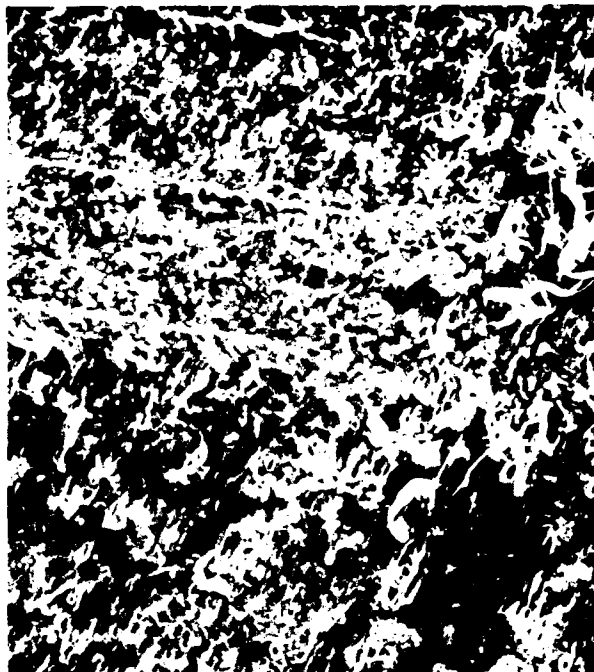
3.  $\times 2000$ .

*d. In 1.0 activity solution.*

*Figure B2 (cont'd). Scanning electron microscope photos of PVC after 8 days.*



1.  $\times 30$ .



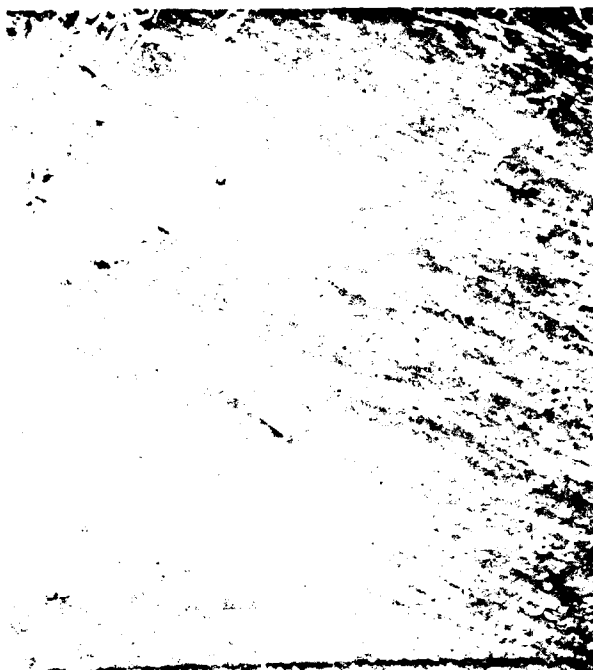
2.  $\times 200$ .



3.  $\times 2000$ .

*a. In 0.0 activity solution.*

*Figure B3. Scanning electron microscope photos of PVC after 15 days.*



1.  $\times 30$ .



2.  $\times 200$ .



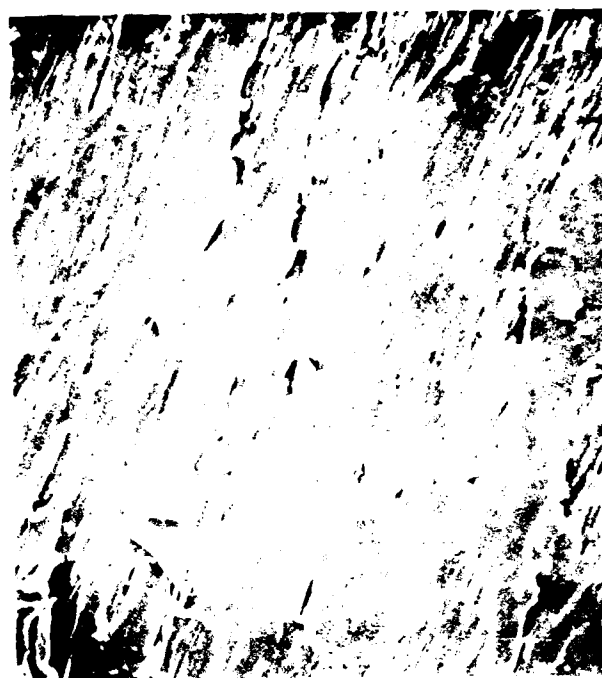
3.  $\times 2000$ .

*b. In 0.2 activity solution.*

*Figure B3 (cont'd). Scanning electron microscope photos of PVC after 15 days.*



1.  $\times 30$ .



2.  $\times 200$ .



3.  $\times 2000$ .

*c. In 0.6 activity solution.*

*Figure B3 (cont'd).*



1.  $\times 30$ .



2.  $\times 200$ .



3.  $\times 2000$ .

*d. In 1.0 activity solution.*

*Figure B3 (cont'd). Scanning electron microscope photos of PVC after 15 days.*



1.  $\times 30$ .



2.  $\times 200$ .



3.  $\times 2000$ .

*a. In 0.0 activity solution.*

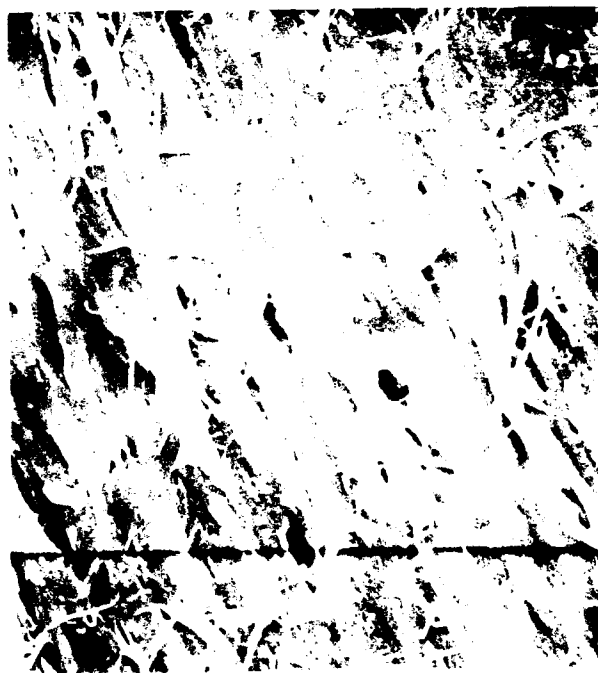
*Figure B4. Scanning electron microscope photos of PVC after 22 days.*



1.  $\times 30$ .



2.  $\times 200$ .



3.  $\times 2000$ .

*b. In 0.2 activity solution.*

*Figure B4 (cont'd). Scanning electron microscope photos of PVC after 22 days.*

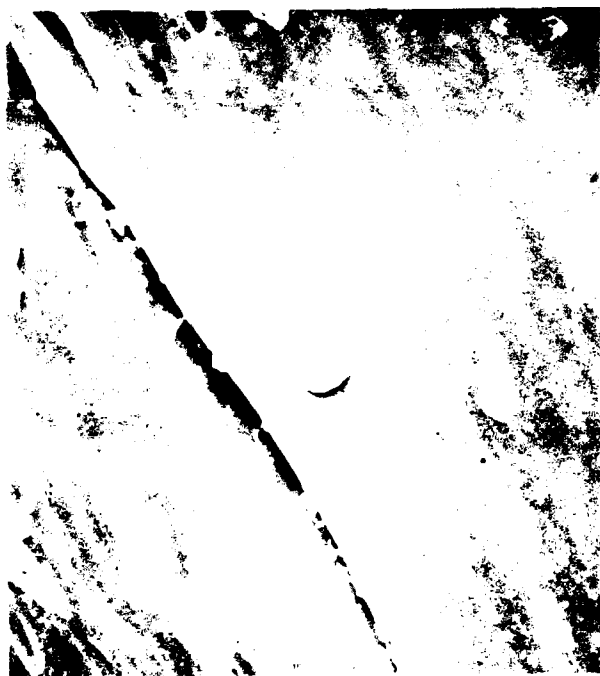




1.  $\times 30$ .



2.  $\times 200$ .



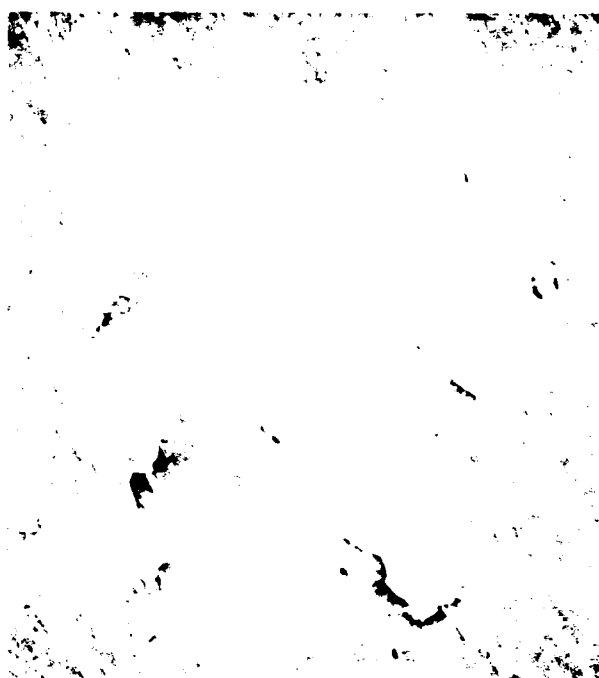
3.  $\times 2000$ .

*c. In 0.6 activity solution.*

*Figure B4 (cont'd).*



1.  $\times 30$ .



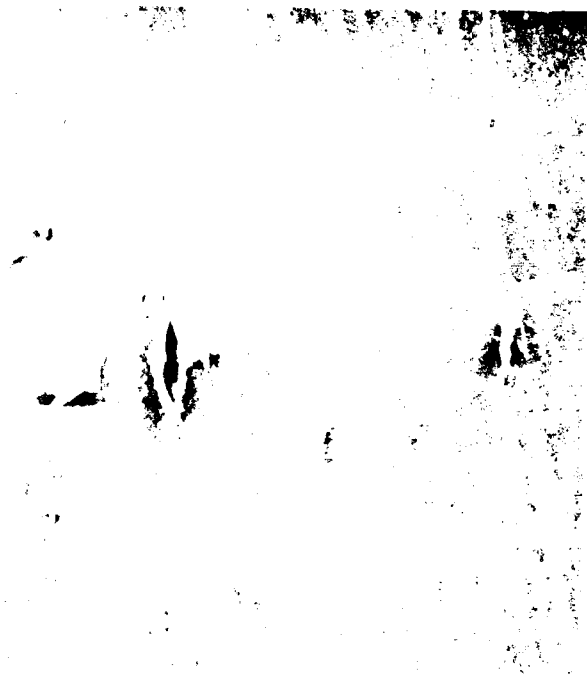
2.  $\times 200$ .



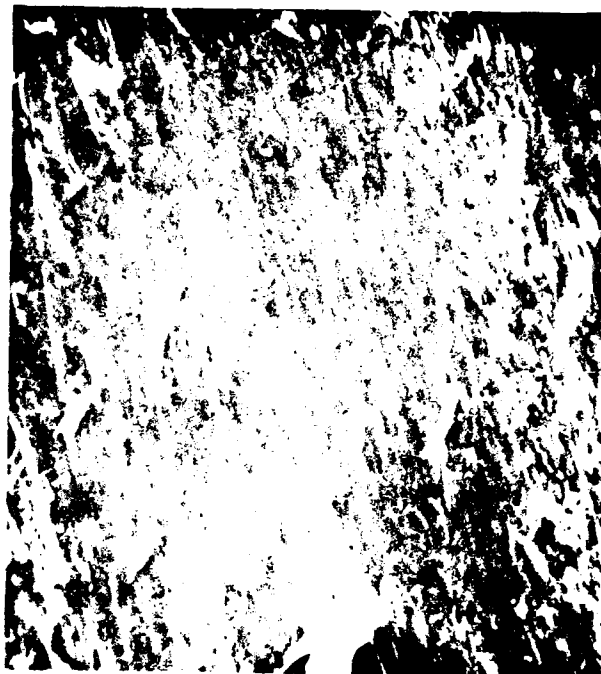
3.  $\times 2000$ .

*d. In 1.0 activity solution.*

*Figure B4 (cont'd). Scanning electron microscope photos of PVC after 22 days.*



1.  $\times 30$ .



2.  $\times 200$ .



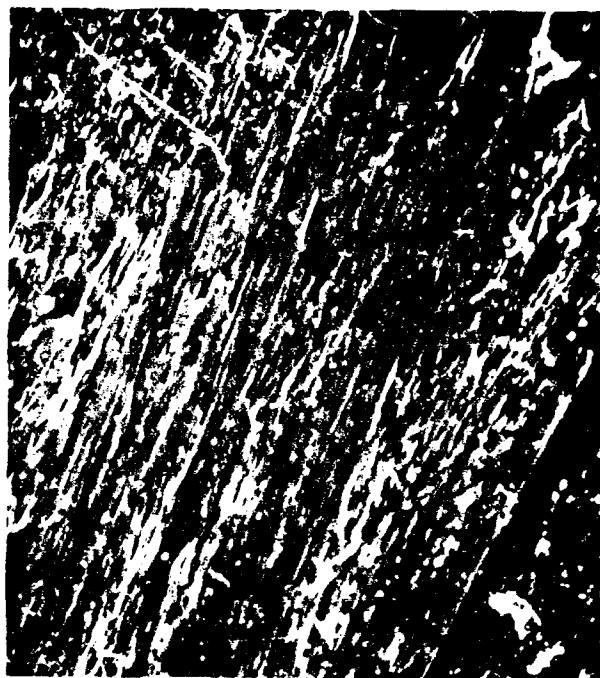
3.  $\times 2000$ .

a. In 0.0 activity solution.

Figure B5. Scanning electron microscope photos of PVC after 33 days.



1.  $\times 30$ .



2.  $\times 200$ .



3.  $\times 2000$ .

*b. In 0.2 activity solution.*

*Figure B5 (cont'd). Scanning electron microscope photos of PVC after 33 days.*



1.  $\times 30$ .



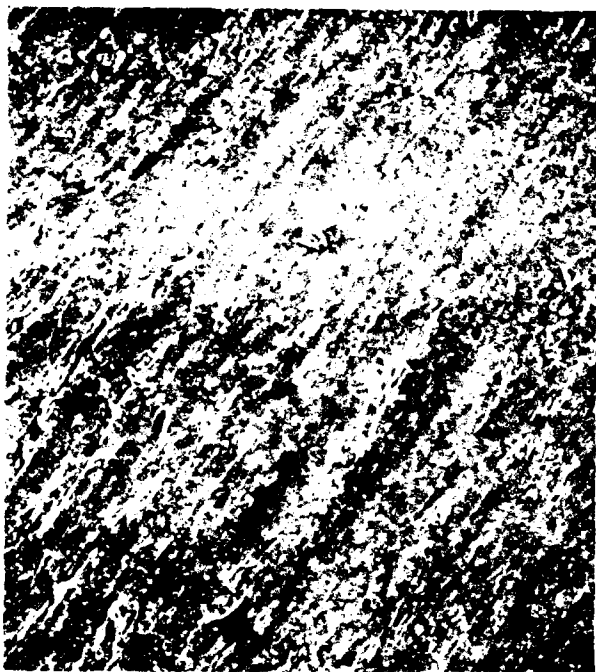
2.  $\times 200$ .



3.  $\times 2000$ .

*c. In 0.6 activity solution.*

*Figure B5 (cont'd).*



1.  $\times 30$ .



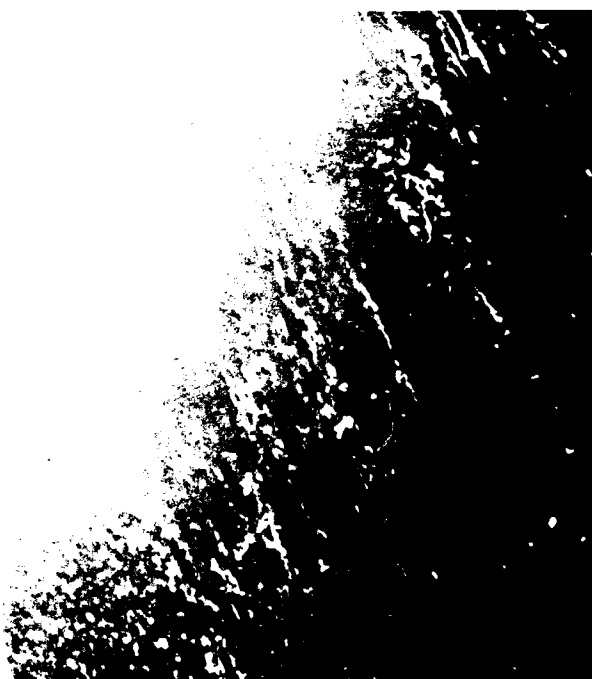
2.  $\times 200$ .



3.  $\times 2000$ .

*d. In 1.0 activity solution.*

Figure B5 (cont'd). Scanning electron microscope photos of PVC after 33 days.



1.  $\times 30$ .



2.  $\times 200$ .

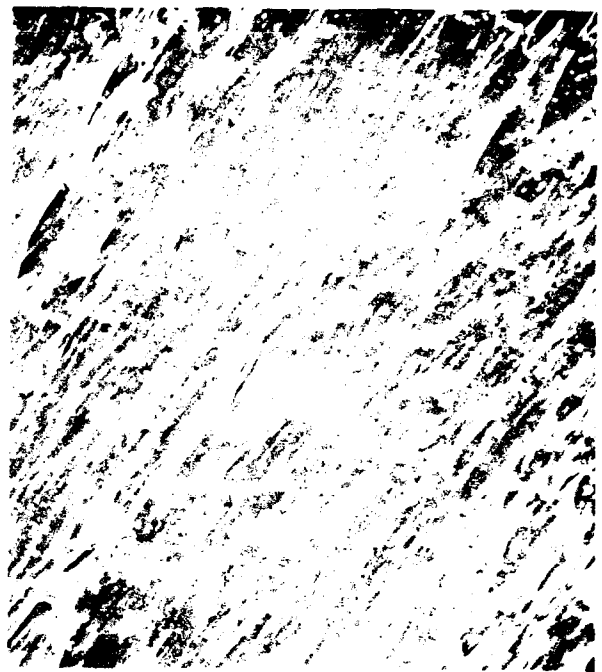
3.  $\times 2000$ .

*a. In 0.0 activity solution.*

*Figure B6. Scanning electron microscope photos of PVC after 68 days.*



1.  $\times 30$ .



2.  $\times 200$ .

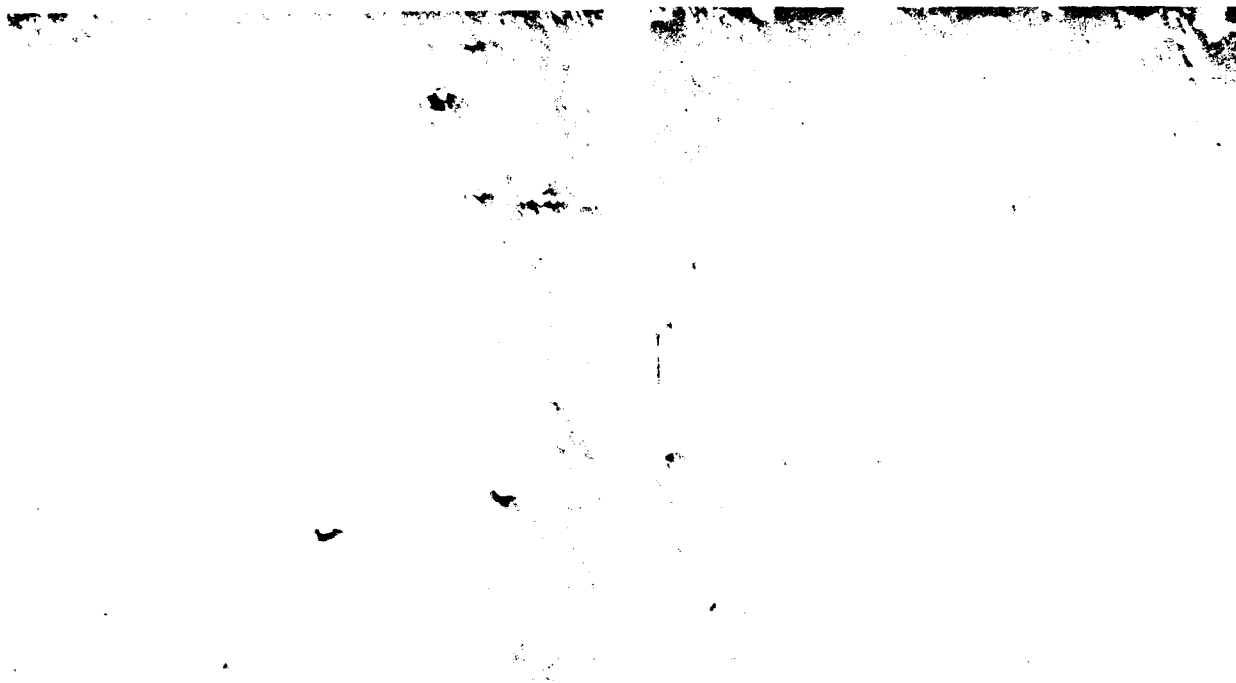


3.  $\times 2000$ .

*b. In 0.2 activity solution.*

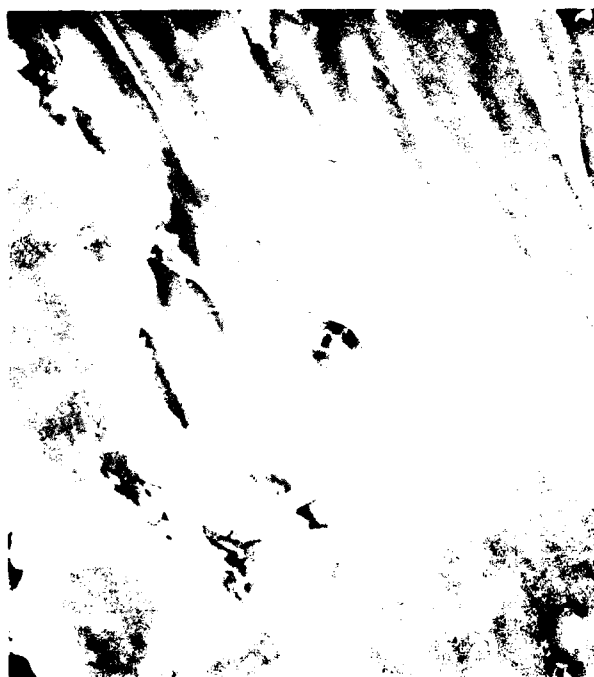
Figure B6 (cont'd). Scanning electron microscope photos of PVC after 68 days.





1.  $\times 30$ .

2.  $\times 200$ .



3.  $\times 2000$ .

*c. In 0.6 activity solution.*

*Figure B6 (cont'd).*



1.  $\times 30$ .



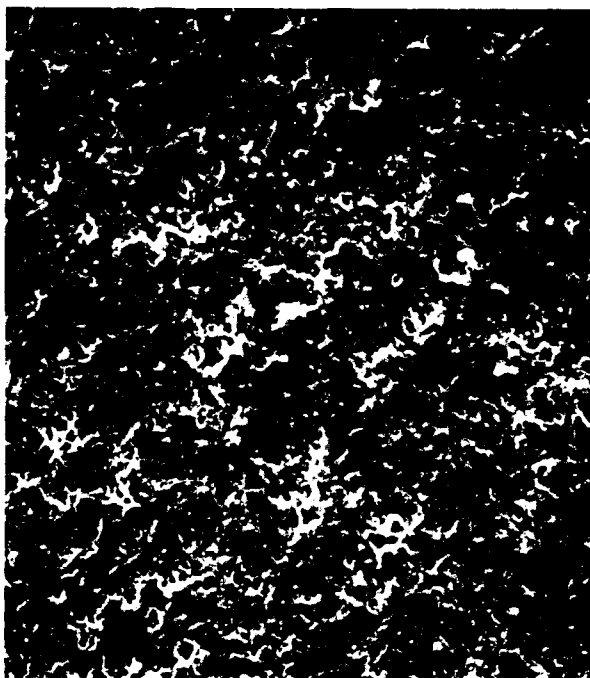
2.  $\times 200$ .



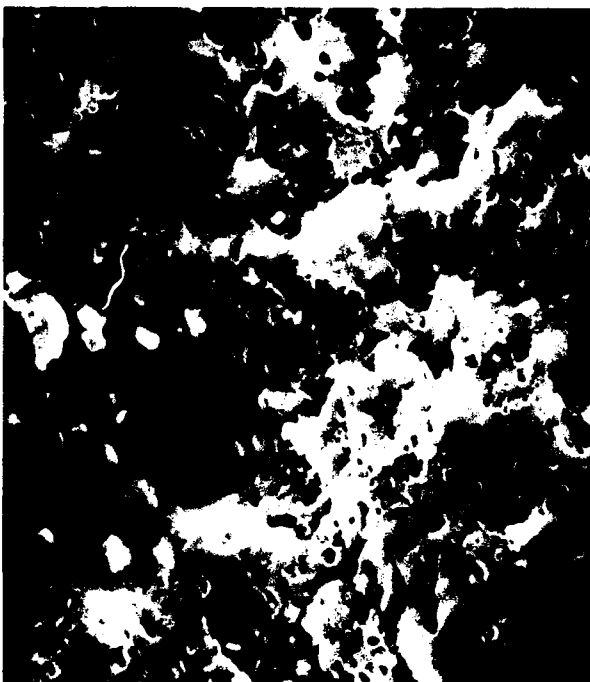
3.  $\times 2000$ .

*d. In 1.0 activity solution.*

*Figure B6 (cont'd). Scanning electron microscope photos of PVC after 68 days.*

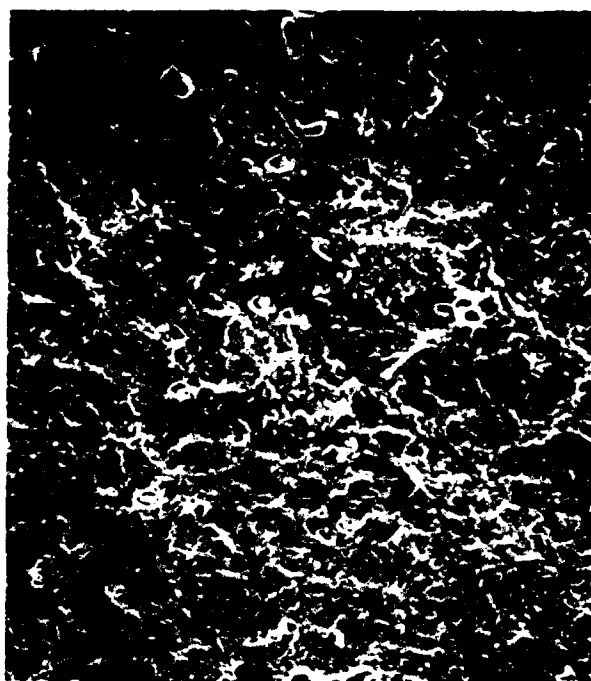


*a. x30.*



*b. x2000.*

*Figure B7. Scanning electron microscope photo of PVC  
in pure methylene chloride after 15 minutes exposure.*



*a. ×30.*



*b. ×2000.*

*Figure B8. Scanning electron microscope photo of PVC in pure methylene chloride after 30 minutes exposure.*

# REPORT DOCUMENTATION PAGE

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, N.H. 03755-1290				8. PERFORMING ORGANIZATION REPORT NUMBER Special Report 92-12	
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